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Study on treatment and recycling of mercury from waste mercury catalysts in China

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Abstract

CCP PVC production is the unique technology in China that consumes most mercury with annual consumption of nearly 10,000 t, about 70% of them entering waste mercuric chloride catalyst. The main supply of mercury for CCP PVC industry includes the production of primary mercury and recycling of waste mercuric chloride catalyst. The production of primary mercury will be constrained and phased out after the Minamata Convention on Mercury going into effect. Therefore, the recycling of waste mercuric chloride catalysts will be an important supply source of mercury before the phasing out of mercury in CCP PVC industry. Based on the investigation of current status of CCP PVC production and recycling of waste mercuric catalysts industry, this paper analyzes mercury content of waste mercuric chloride catalysts and mercury recycling rate of waste mercury catalyst recycling industry, and estimates less than 50% of cyclic use of mercury in CCP PVC industry. In view of low cyclic use rate of mercury and excessive production capacity of the industry, this paper puts forward policy recommendations in the following three areas such as strict implementation of mercury destiny reporting system, stricter management of environmental access conditions and demonstration and extension of close loop circulation mechanism of mercury.

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Keywords: waste mercury catalysts, treatment and recycling of mercury, China

CCP PVC production is the unique technology in China with the biggest consumption of mercury. As the catalyst for the process of synthesizing VCM by acetylene and HCl, mercuric chloride catalyst is employed in large amount in CCP PVC industry. It is turned into waste mercury catalysts in the production process due to drop and final loss of activity because of factors such as mercury sublimation and poisoning. At present, this industry discards waste

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mercury catalysts as many as about 15,000 t each year, containing several hundred tones of mercury with relatively high value for recycling and reuse. Therefore, recycling and disposal of waste mercury catalyst becomes a relatively mature industry in our country.

The Minamata Convention on Mercury was adopted by the international communities in 2013 and is expected to go into effect as of 2016. The Minamata Convention on Mercury requires prevention and control the whole cycle risks of the production, use, release and waste of mercury. The CCP PVC production is the key mercury consumption technology subject to the regulation of the Convention. Although the Convention does not set a specifically phasing out deadline, it requires that all parties should ban the construction of new primary mercury mines after the Convention going into effect and close all primary mercury mines within 15 years. Mercury supply in China mainly comes from the production of primary mercury. The regulation of the Convention on primary mercury means the control of the source of mercury supply for CCP PVC production. Therefore, the recycling and treatment of waste mercury catalysts will become an important source of mercury supply before the phasing out of mercury consumption by CCP PVC industry in our country. Our country should strengthen the management of recycling of waste mercury catalysts, raise recycling rate of mercury, and minimize mercury release and secondary pollution in mercury recycling process.

1. Waste mercury catalyst recycling and treatment technology and mercury release

1.1. Key processes for recycling and disposal of waste mercury catalysts

Mercury in waste mercury catalysts mainly exists in the form of mercuric chloride, with small amount of reduced elemental mercury at the same time. The following three processes could be employed for recycling and treatment of waste mercury catalysts: recycling metal mercury by distillation, recycling mercuric chloride by oxygen-control dry distillation method and regenerated mercuric chloride catalyst by chemical activation method.

Recycling of metal mercury by distillation is a traditional mercury reclamation process for waste mercury catalysts, mainly including the processes such as chemical retting, roasting and condensation. Mercuric chloride in waste mercury catalysts is turned into mercury oxide through chemical retting. Metal mercury is obtained after the processes such as roasting and condensation. The transformation degree of mercuric chloride determines the mercury recycling rate [1].

Oxygen-control dry distillation method is a new technology that recycles $HgCl_2$ and active carbon in waste mercury catalysts. Applying the fact of coking temperature of activated carbon higher than that of sublimation temperature of $HgCl_2$ and the theory of easy sublimation of $HgCl_2$ at high temperature, we put dried waste mercury catalyst in an airtight furnace that could rotate and adjust temperature. The mercuric chloride in the feed will turn into vapor. We could extract it by a gas extraction device, strongly cool it into solid particles and then recycle them.

With the prerequisite of no separation of activated carbon with mercuric chloride in waste mercury catalysts, chemical activation method employs chemical method to reactivate active carbon, eliminates accumulated carbon and catalyst poisoning, and then adds appropriate amount of addictive and active substance based on the requirement for mercuric chloride content in catalyst product-mercuric chloride to achieve the reclamation or generation. The process flow is as the follows: firstly remove mechanical impurities (such as iron fillings, screws, stones and wood block) in waste mercury catalysts and fine waste mercury catalysts by manual selection (or machine selection) and screening, then put it in an activator for chemical activation, followed by production according to normal mercury catalysts production process.

The investigation results show that at present, most enterprises employ the technology of recycling metal mercury by distillation method. Only a few enterprises employ oxygen-control dry distillation method. There is not any enterprise that employs chemical activation method.

1.2. Mercury release in the recycling and disposing process

All processes of metallic mercury recycling technology by distillation method will release mercury at different degrees. Figure 1-1 shows the release path. In the chemical dipping process, waste mercuric catalysts firstly is dipped in alkaline solution, then heated and dried by high temperature vapor, turning mercuric chloride into

mercuric oxide. This process will generate mercury-containing waste gas and mercury-containing wastewater. In roasting process, the treated waste mercury catalysts are put into a distilling furnace, heat it to 700～800℃, mercuric oxide in the catalysts will decompose into mercury vapor. This process will generate waste gas and solid waste that contain mercury. In condensation process, mercury vapor will enter condensation system through the mercury collection box, most mercury vapor will quickly be condensated and becomes metal mercury in liquid form, they will become metal mercury product after processing, this process will generate waste gas containing mercury. In case of less mercury but more dust in the fume entering the condenser, crystal nucleuses are usually formed resulting from mercury vapor condensation. If the flow speed of the smoke is relatively fast with relatively fast condensation, the crystal nucleuses will form fine metal mercury beads. It is hard for these mercury beads to concentrate and merge. Rather, they will combine with precipitated mine dust, coal ash and carbon particles to generate mercuric soot with mercury content usually < 2%. The mercuric soot usually will be roasted again.

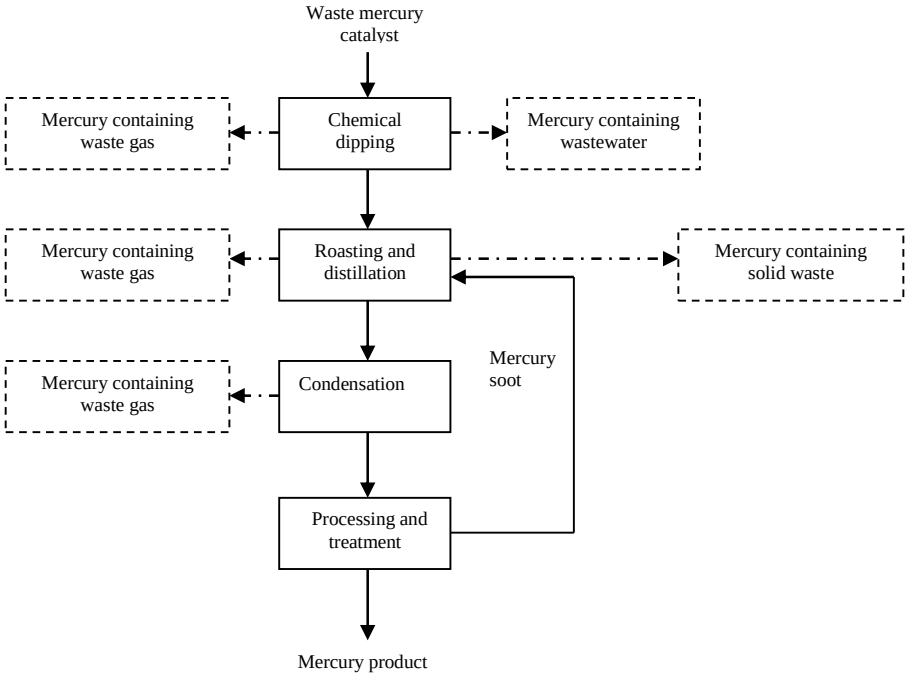

Fig. 1. Mercury release path of recycling of waste mercury catalysts by distillation process

In the real production process of CCP PVC, if the controlled proportion of HCl to acetylene is not appropriate, excessive acetylene will reduce mercuric chloride to elemental mercury adsorbed in the surface of catalyst [2-3], there exists elemental mercury in waste mercury catalysts[4]. In the process of application of oxygen-control dry distillation method, the mercury possibly in waste mercury catalysts is turned into vapor, and enters the follow-up treatment facilities with mercuric chloride vapor. Compared with the traditional technology on recycling of waste mercuric catalysts, this technology directly turns mercuric oxide into vapor and recycles mercuric chloride in waste mercury catalysts. It avoids change of working process, reuses activated carbon, and reduces the release of waste activated carbon and other residues that contain mercury.

2. Mercury recycling rate and current status of cyclic use of mercury in the industry

2.1. Mercury content in waste mercury catalyst

Waste mercury catalysts recycled and disposed by enterprises usually is composed of waste mercury chloride catalysts, waste activated carbon in mercury removing device and mercury-containing sludge resulting from treatment of mercury-containing wastewater by CCP PVC enterprises.

The content of mercuric chloride of waste mercury catalysts varies with the type of mercury catalysts. Mercury catalyst with 7%~9% of mercuric chloride is the intermediate mercury concentration catalyst and 10.5%~12% of mercuric chloride is high mercury concentration catalyst. In general, the mercuric chloride concentration of the above waste catalysts is about 4%. Mercury catalyst with mercuric chloride content at 4%~6.5% is low mercury catalyst, after application, their concentration of mercuric chloride is only about 2%[5-6]. At present, CCP PVC industry is in the transition period of low mercury catalysts replacing high mercury catalysts. Among waste mercuric chloride catalysts, there are both high mercury concentration and low concentration mercury. In general, the treatment enterprises do not distinguish the waste catalysts with high or low mercury concentration. Therefore, there is relatively big change of mercuric chloride content in waste mercuric chloride catalysts. The total mercury content determination of 23 waste mercury catalyst samples from CCP PVC production enterprises and waste mercury catalyst recycling enterprises collected in 2014 finds the range of mercuric chloride equivalent at 0.54%~6.07% with the average at 3.14%. Figure 1-2 shows the mercuric chloride content of the samples of waste mercury catalyst.

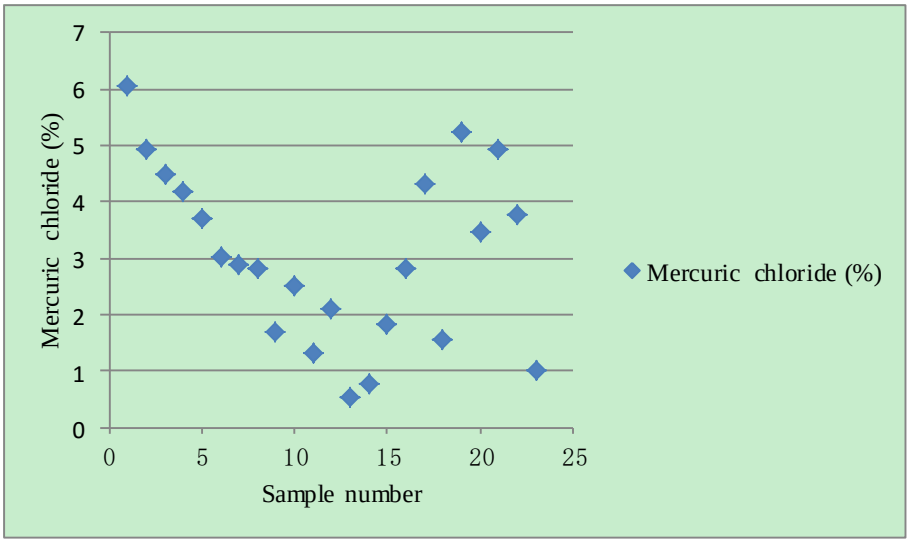

Fig. 2. Mercuric chloride content of waste mercury catalysts

There is relatively big change of the mercuric chloride content of waste activated carbon in mercury removing device. The determination results reported by some CCP PVC manufacturing enterprises range between 1.0% and 10.4%, this has something to do with the application time of activated carbon. Because the activated carbon in mercury removing device is the $HgCl_2$ sublimate adsorbed on course chloroethylene released at high temperature, the longer the application time of activated carbon, the higher the mercuric chloride content in waste activated carbon. In general, CCP PVC production enterprises replace activated carbon once in every 6 to 12 months, this also leads to relatively big differences of mercuric chloride content in waste activated carbon.

In the CCP PVC production process, sodium sulfide precipitation and multi-stage intermittent reaction of flocculent are usually employed to treat mercury containing wastewater. The mercury containing wastewater has complex composition, there are mercury compounds in many forms, metallic mercury and other organic substances and ions. After treatment, the mercury content of mercury containing sludge usually is 0.24% ~ 0.47%.

2.2. Mercury recycling rate of waste mercury catalyst recycling technology

Mercury recycling rate of mercury recycling technology by distillation method refers to the percentage of elemental mercury amount recycled from waste mercury catalyst to total amount of mercury in waste mercury catalyst.

According to the national investigation in 2011 and 2013 on current status of mercury pollution sources and the data reported by relevant enterprises during the check on prevention and control of mercury pollution, 6 groups of data reported by different enterprises that recycle mercury by distillation technology in their normal operation in 2010 and 2012 are chosen as samples to estimate mercury recycling rate. The results are shown in Table 1-1. The data of the table shows the mercury recycling rate of mercury recycling technology by distillation method ranging from 97.09% to 99.97%. The mercury recycling rate resulting from weighted average treatment amount of waste mercury catalysts is 98.55%, basically consistent with the mercury recycling rate estimated by other studies [7]. The mercuric chloride content of each batch of waste mercuric catalyst collected by each enterprise is different, the average mercuric chloride content of these enterprises is 2.22%~3.04% and there is no evident correlation between mercuric chloride content and mercury recycling rate.

Table 1-1 Mercury recycling rate of waste mercury catalyst by distillation method

Sample amount	Treatment *(t)*	Average mercuric chloride content *(%)*	Mercury content *(t)*	Mercury recycling amount *(t)*	Mercury recycling rate *(%)*
1	3622.00	2.74	99.20	97.70	98.49
2	3080.00	3.04	93.50	92.80	99.25
3	1281.60	2.07	26.50	26.40	99.62
4	287.00	2.44	7.01	6.98	99.57
5	3603.39	2.74	98.66	95.79	97.09
6	1500.00	2.22	33.30	33.29	99.97

Oxygen-control dry distillation method is the demonstration and extension technology identified in the 2010 Program of Ministry of Industry and Information Technology on Comprehensive Prevention and Control of Mercury Pollution of CCP PVC Industry [8]. At present, only one enterprise in the country utilizes it. The mercury recycling rate by recycling of mercuric chloride and activated carbon is 99.1%[3]. Mercury recycling rate of oxygen-control dry distillation method increases by 0.5% compared with that of distillation method. Because of relatively large amount of waste mercury catalyst, the application of oxygen-control dry distillation method for all such waste catalysts could recycle several tones more mercury each year and also may reduce mercury release to a certain extent.

Uncertainty of estimate

Waste mercury catalysts collected by recycling enterprises include both high mercury catalyst and low mercury catalyst. There is relatively big change of mercury content among different batches of waste mercury catalysts; and the analysis and determination capacity of relevant enterprises is limited. Therefore, it is difficult to accurately estimate mercury content and mercury recycling rate of waste mercury catalysts. It is therefore important in the future to do a more thorough investigation of the Hg content and mercury recycling rate of waste mercury catalysts.

2.3. Mercury recycling rate of waste mercury catalyst recycling industry

The mercury recycling rate of waste mercury catalyst recycling industry refers to the percentage of total recycled amount of mercury from waste mercury catalyst recycling industry against total mercury consumption of CCP PVC industry. Among them, the total mercury consumption of CCP PVC industry is estimated by the equivalent mercury amount of total consumption of mercuric chloride for production of mercuric chloride catalysts each year.

The mercury recycling of waste mercury catalyst recycling and treatment enterprises across the country with license during 2010~2014 is shown in Table 1-2. The mercury recycling amount in the Table is the total amount of recycled mercury of relevant enterprises with operation license. Because the 2014 new enterprises with operation

license go beyond the statistic scope, 2014 data in the following table is slightly lower than the national total amount. However, the difference is not big based on the estimate of 2014 output of CCP PVC.

Table 1-2 Mercury recycling of waste mercury catalysts treatment enterprises during 2010~2014

Year	Capacity of treating waste mercury catalyst *(10,000 t)*	Treated amount of waste mercury catalyst *(10,000 t)*	Mercury recycling amount *(t)*
2010	1.5	0.8	179
2011	1.2	0.8	169
2012	1.6	0.8	217
2013	2.0	1.5	267
2014	>3.5	>1.5	>258

Based on the investigation and inspection on prevention and control of mercury pollution organized by Ministry of Environmental Protection over the past few years, Table 1-3 presents the consumption and recycling of mercury of CCP PVC enterprises across the country during 2010~2012. The findings of the investigation show that in 2010~2012, mercury content of solid wastes such as waste mercury catalysts and waste activated carbon generated from CCP PVC industry is about 600~800 t. The findings of past studies show that 40%~98.1% of the mercury in CCP PVC production enters [2,9-11] waste mercury catalysts and waste activated carbon. The investigation findings are basically consistent with the study findings. The output of CCP PVC production of China still grew in 2013 and 2014. However, the total mercury consumption did not have synchronized growth with PVC output because of gradual extension of low-mercury catalyst and reduction of mercury consumption per unit PVC of the industry, basically maintaining at about 800 t.

Table 1-3 Consumption and recycling of mercury of CCP PVC production during 2010~2012

Year	Output *(10,000 t)*	Consumption of mercury catalyst *(10,000 t)*	Mercury content of catalyst *(t)*	Waste amount *(10,000 t)*	Mercury content of waste *(t)*
2010	867.0	1.1	837.3	1.5	603
2011	1006.3	1.4	1015.9	1.6	>520
2012	1178.2	1.7	1086.9	2.0	810

Note: Mercury contents of mercury containing wastes in 2011 only includes the mercury in waste mercuric catalysts and waste activated carbon.

In general, the average annual consumption of mercury of CCP PVC industry of our country is about 800~1000 t. Solid wastes including waste mercury catalyst contain about 600~800 t mercury. However, less than 300 t mercury have been recycled, the overall cyclic use rate of mercury is less than 50%.

3. Problems and Recommendations

3.1. Existing problems

Low cyclic use rate of mercury and seriously excessive production capacity of the industry are the main problems of the enterprises that recycle and treat waste mercury catalysts.

Solid wastes such as waste mercury catalysts, waste activated carbon, mercury containing sludge from treatment of mercury containing wastewater generated from CCP PVC production and other solid waste and packaging

materials contacting with such catalyst belong to HW29 (mercury containing hazardous waste) of the National Catalogue of Hazardous Wastes released by Ministry of Environmental Protection. The transport and movement of these should comply with the Measures on Management of Hazardous Waste Manifests. Annual mercury consumption of CCP PVC industry of our country is about 600~1000 t. Based on the estimated recycling amount of mercury of relevant enterprises with business license, current mercury recycling rate of the industry is less than 50%. Over 50% mercury is released in the processes of production, consumption and waste disposal of catalysts, or flows to the enterprises that recycle and treat waste mercury catalysts without permission. These enterprises go beyond national supervision and usually make mercury with indigenous method, poor facilities, low recycling rate of mercury, heavy emission, and low recycling & disposal cost. In addition, as the mercury content from waste low-mercury catalysts decreases with lower recycling benefit, the low cost operation of illegal enterprises has more advantages.

Excessive production capacity of CCP PVC industry is a long-term problem of this industry. Until now, there is no effective solution and control. And the problems of excessive production capacity of mercuric chloride catalysts and excessive capacity in recycling of waste mercury catalysts gradually emerge. In 2014, production capacity of mercuric chloride catalyst of China was as high as 40000~50000 t, where the actual output was only 11000 t, over 50% of them being excessive capacity. In 2013~2014, there were 4 waste mercury catalyst recycling enterprises with operation license granted by the State and their recycling capacity about 35000 t. In 2014, the authority of review and approval of the operation license was delegated to the local government at province level, the amount of such enterprises went up to over 8 with total treatment capacity exceeding 50,000 t. However, the annual generated amount of waste mercuric catalysts is less than 20,000 t. The treatment capacity far exceeds the market demand, leading to chaos of catalyst market and seriously affecting healthy development of the industry.

3.2. Recommendations on management

- Strict implementation of reporting system for mercury destiny

Huanfa No.[2013]119 Document of Ministry of Environmental Protection requires implementation of the system reporting the destiny of mercury in the industries with intentional production or use of mercury and other relevant industries. The Document requires that primary mercury production enterprises, CCP PVC production enterprises and relevant enterprises manufacturing mercury-added products shall before the end of March of each year report to environmental protection department of its mercury destiny of last year, including the data such as utilization and consumption of mercury, generation, movement and disposal of mercury containing waste; generation and release of mercury pollutants; sources of mercury related raw materials and destiny of products. With the implementation of mercury destiny reporting system, we could understand the data of utilization, consumption, release and recycling of mercury of CCP PVC production and relevant industries and its change. With these data as bases, the government could control chaotic flow of mercury among relevant industries, monitor the movement and disposal of waste mercury catalysts and curb environmental infringements such as illegal treatment of waste mercury catalyst and making mercury by indigenous method.

- Enhance the management of environment access conditions for waste mercury catalyst recycling industry

In order to effectively control excessive capacity in treating and recycling of waste mercury catalysts, it is recommended that China should study and identify environment access conditions for waste mercury catalyst recycling industry; make stricter access conditions in terms of production capacity, development of production equipment and environmental protection facilities; build the capacity in determination and analysis of mercury; raise mercury recycling rate; require local environmental protection departments to make strict conditions for review and approval of business license for waste mercuric catalysts and curb chaotic expansion of waste mercury catalyst recycling industry. It is recommended that China should strengthen follow-up supervision after granting license, establish random inspection system for the enterprises with operation license and accelerate the phasing out of outdated production capacity.

- Extend the close loop circulation mechanism of mercury

Because of lack of management or difficulty in management of the movement or marketing of mercury among different industries, some waste mercury catalysts enter the enterprises treating waste mercury catalyst against law or are mixed with high-mercury catalyst but sold as low-mercury catalyst, this severely affects recycling and reuse of mercury. Therefore, it is recommended that Ministry of Environmental Protection should encourage and support the establishment of closed loop circulation of mercury among the three industries; establish the technical alliance on prevention and control of mercury pollution with upstream and downstream enterprises as the core; achieve orderly movement and marketing of mercury among the enterprises in the alliance; standardize internal management of enterprises; apply and extend advanced technology; improve the capacity in reducing mercury emission and recycling capacity of relevant enterprises and raise recycling rate of mercury.

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